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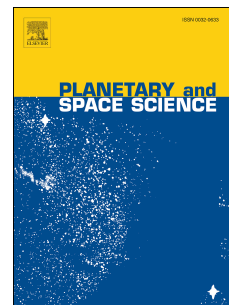
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# Accepted Manuscript

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**D/H Fractionation during Sublimation of Water Ice at Low Temperatures into a Vacuum**

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**Abstract**

The study outlined in this article was carried out within the framework of ESA's PROSPECT programme, which will provide both a sample drill and miniaturised mass spectrometer system for flight on-board the planned Russian Luna-27 mission to the lunar south pole. There, it aims to collect samples of regolith, containing water ice and other volatiles, and to make isotopic and abundance measurements to fingerprint the source(s) of these volatile species. However, it is necessary to first consider how any localised temperature increases during sample acquisition activities may result in water ice loss *via* sublimation and thus isotopic modification of the remaining residual ice.

To attempt to address these concerns, a suite of sublimation experiments was conducted at the Laboratoire de Géologie de Lyon, where a method for performing such experiments was already established (Lécuyer et al., 2017). The results of this work will help to inform modelling which will extrapolate the data down to lunar-relevant conditions.

**Keywords:** Moon; Sublimation; Fractionation; Water; PROSPECT.

**1. Introduction**

Over the course of the last decade, a renewed interest in the exploration of the Moon has led to the discovery and characterisation of previously unknown volatile reservoirs both in the Moon and at its

surface (e.g. Barnes et al., 2014; 2016; Füri et al., 2012, 2014, 2015; Greenwood et al., 2011; Hashizume et al., 2000; McCubbin et al., 2010; Mortimer et al., 2015, 2016; Saal et al., 2008; Tartèse et al., 2013, , with abundances of water in the lunar interior possibly even reaching terrestrial-like values (e.g. Boyce et al., 2010; Hauri et al., 2011; McCubbin et al., 2015 and references therein). In addition to volatiles locked up in mineral phases in returned Apollo samples, spectroscopic measurements by a range of orbiting spacecraft have revealed the presence of hydrogen across the lunar surface, but particularly concentrated in colder regions near to the poles and in permanently shadowed craters (Clark, 2009; Feldman et al., 1998; Mitrofanov et al., 2010; Nozette et al., 1996; Pieters et al., 2009; Sunshine et al., 2009). Specifically, the LCROSS mission in 2010 detected  $5.6 \pm 2.9$  wt.% water, present as ice, in the ejecta plume thrown up by a spent rocket section acting as an impactor into the south polar Cabeus crater (Colaprete et al., 2010).

However, what remains unknown is the source(s) of this water ice, its exact abundance, and its form (i.e. does it form thin rims of ice around individual grains, dispersed throughout the upper metres of regolith, or it is concentrated into thicker water ice lenses at certain depths?). These are key questions for several different reasons. Firstly, from a purely scientific viewpoint, fingerprinting the source of water on the lunar surface would reveal new information about the delivery of volatiles to the Earth-Moon system and thus the development of telluric atmospheres. Secondly, water is important for the purposes of *in-situ* resource utilisation (ISRU); water can be used to sustain life in a future scenario where a permanent Moon base or ‘Moon village’ is envisaged, or it can be split up into H and O, for use as fuels or as air to support such human exploration beyond the confines of low Earth orbit (LEO).

To attempt to address these questions about lunar surface water and its ISRU potential, the European Space Agency (ESA) are developing the PROSPECT package to fly to the southern region of the Moon on board Russia’s Luna 27/Luna Resurs mission in the early 2020s.

PROSPECT contains both a sample drill arm (ProSEED) to collect samples of regolith from depths of up to 2 m below the lunar surface, and transfer them to a miniaturised chemical laboratory (ProSPA), where the samples will be heated up to 1000 °C in the presence of different reagent gases to extract a range of different volatile species, including water.

Whilst the drilling, sample extraction/transfer, and pre-analysis imaging procedures have been designed to ensure the volatile-containing samples are never exposed to temperatures above -150 °C, given the ultra-high vacuum conditions present at the lunar surface, it is necessary to understand first the rate of water ice sublimation to avoid the risk of an initially volatile-bearing sample losing all of its water ice content during the sample extraction and transfer time window. Further, if only part of the water ice is lost *via* sublimation, does that loss introduce any hydrogen isotopic fractionation and thus make isotopic analysis of the residual ice sample inconclusive?

## 2. Experimental Procedure

Although it was not possible to mimic true lunar surface temperatures and pressures in the laboratory setting for these experiments, a range of temperatures and pressures at which sublimation was possible were chosen for investigation, with the view to using the results from this study to inform or 'ground-truth' modelling of water ice sublimation under the lower temperature and higher vacuum conditions that the real lunar regolith samples will experience.

An initial batch of tests was carried out at -75 °C, under the pre-existing pressure conditions in the extraction line (where the baseline pressure of the line between sublimation experiments was around  $10^{-3}$  mbar). Several experiments were also made at different temperatures at these pressure conditions, across the temperature range -100 °C to -40 °C. A second batch of experiments was then conducted at -100 °C, after modifications to the laboratory set-up permitted a lower baseline pressure ( $10^{-5}$  mbar) to be reached. A change of method from static to dynamic vacuum pumping during sublimation, coupled with cryopumping using a u-shaped liquid nitrogen cooled trap, also enabled a lower pressure to be maintained in the line as sublimation progressed, preventing saturation of the volume by more efficiently removing water already in the vapour phase and thereby allowing further sublimation to occur.

A third batch of experiments was carried out to assess the effect of changing pressure at constant temperature, with new experiments at -75 °C under the lower pressure of  $10^{-5}$  mbar, to compare with tests conducted previously.

Isotopic compositions of sublimate and residue waters (-75 °C experiments)/residue waters only (-100 °C experiments) were measured in several batches using an on-line Cr reduction method (Morrison et al., 2001) in a EuroEA3028-HT elemental analyser, connected to an IsoPrime IRMS. Isotopic data are herein expressed using the delta notation, as parts per thousand deviations from the international standard Vienna Standard Mean Ocean Water (VSMOW). Isotopic values for individual samples are the averages of analyses of multiple aliquots of the same sample ( $n = 2-7$ ). Where several experiments have been conducted under the same conditions, the averages of these values are occasionally presented; where this is the case, it has been noted in the relevant figure caption or the text.

For all experiments, the same starting water reservoir was used, and its composition remeasured alongside each batch of samples to take into account any isotopic evolution over time within the starting water reservoir. The sublimation experiments themselves were conducted following the method previously outlined in Lécuyer et al. (2017), thus:

- A 0.5 mL aliquot of water was measured out from the reservoir flask of starting water (doubly-distilled Rhône river water) using a micropipette, transferred into a small Pyrex<sup>TM</sup> glass round-bottomed vessel for weighing (using a balance accurate to  $\pm 0.0001$  g), and then introduced into the vacuum system.
- Before exposing the water aliquot to vacuum, the water inside the round-bottomed vessel was frozen using a bath of liquid nitrogen (LN). Once frozen, the vessel was opened to the vacuum line and pumped down to the appropriate pressure.
- Then, the vacuum line was isolated from the pumps and the temperature-controlled cryogenic trap (TCCT) was cooled (again with an external bath of LN), ready for the transfer of the water aliquot (see Figure 1 for a schematic diagram of the TCCT set-up). Water transfer into the TCCT was facilitated by the use of a hand-held heat gun.
- After water transfer was complete (monitored by watching the pressure of the vacuum line fall as water vapour was trapped down into the TCCT), the vacuum line was again opened to the pumps to ensure full removal of all untrapped vapour from the system. After

approximately ten minutes, the line was again isolated from the pumps, ready for sublimation to begin.

- Temperatures of sublimation were controlled by use of a thermal resistance heating wire coiled around the sample tube inside the TCCT, balancing out the cooling effect of an external bath of liquid nitrogen, and with efficient heat transmission ensured by an envelope of helium gas between the LN bath and the heating coil/sample tube (Fig. 1). Temperatures were monitored in real-time by use of a thermocouple positioned at the lowest point of the TCCT. Once the desired temperature was reached, the temperature was able to be held at a relatively constant value, accurate to within  $\pm 2$  °C of the target temperature.
- During sublimation, a separate pre-weighed empty Pyrex<sup>TM</sup> vessel with a glass valve was cooled using a bath of LN, for trapping of any water vapour released during sublimation (the 'sublimate'). This process was repeated after sublimation by heating up the TCCT to 30 °C and collecting all of the residual ice as vapour in a third pre-weighed empty Pyrex<sup>TM</sup> vessel.
- Amounts of sublimate and residue were then calculated by re-weighing the now-full valved collection vessels and subtracting their empty weights.
- Finally, both sublimate and residue water fractions were transferred into small (1 µL) glass vials using separate syringes, stored in an oven at 60 °C between uses, and sealed with metal caps containing septa for introduction into the autosampler of the Elemental Analyser for D/H measurement.

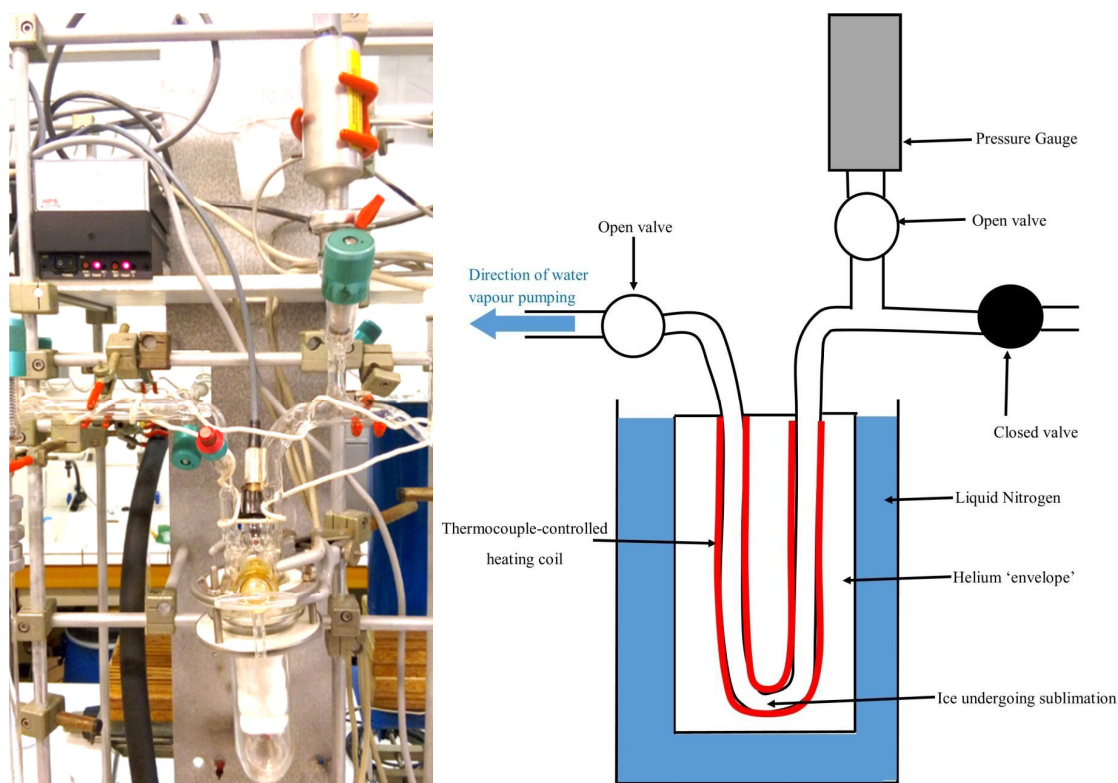


Figure 1: TCCT Section of Vacuum Line

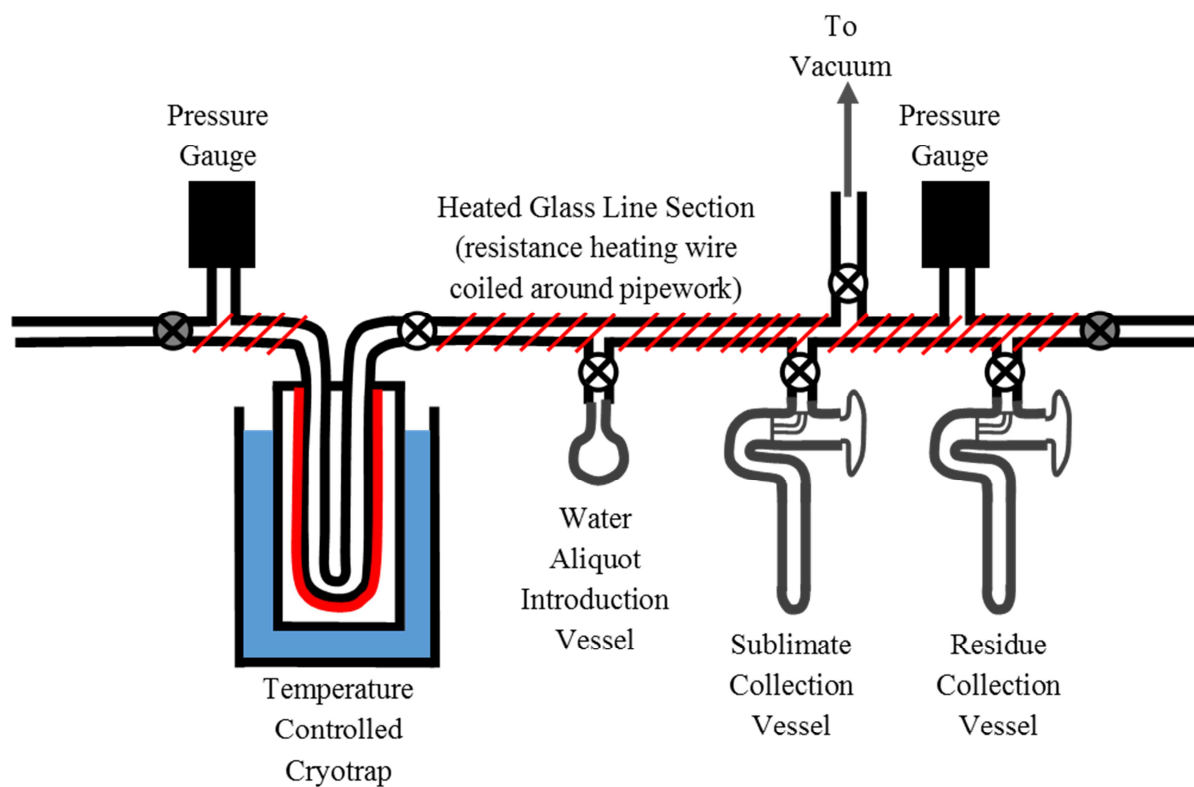


Figure 2: Schematic diagram of the glass vacuum line set-up used for sublimation experiments



Water recovery yields were monitored for the first ten samples to ensure that no significant loss of water was occurring as a result of the experimental method, and were calculated using equation 1:

**Equation 1:** 
$$\text{Recovery Yield} = \frac{(\text{Sublimate}_{\text{mass}} + \text{Residue}_{\text{mass}})}{\text{Initial Water}_{\text{mass}}} \times 100$$

With an average recovery yield of 99.64 % (Figure 3), and only one experiment (the first to be conducted, at 5 minutes duration) having a yield of less than 99 %, it can be concluded that the transfer of water vapour around the vacuum line using a series of cryotrap, heating guns, and heating wire does not result in significant mass loss.

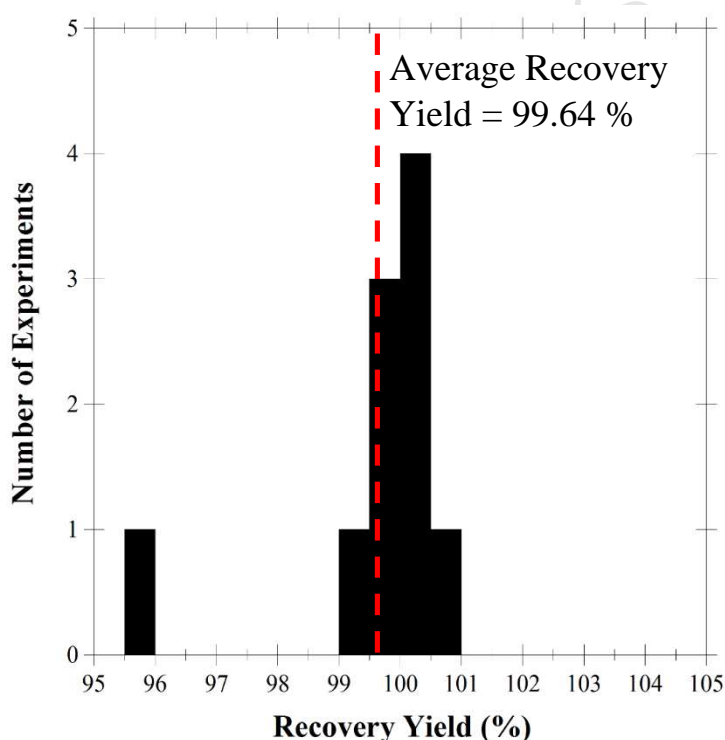


Figure 3: Recovery yields for individual experiments conducted at -75 °C.

Similarly, the isotopic mass balance of the recovered water was compared to the initial composition of the water aliquot used, and this was calculated using equation 2:

**Equation 2:** 
$$\delta D_{\text{initial}} = \delta D_{\text{mix}} = \frac{(\%_{\text{sublimate}} \times \delta D_{\text{sublimate}}) + (\%_{\text{residue}} \times \delta D_{\text{residue}})}{100}$$

Using this equation, an average  $\delta D$  value of  $-72.73 \pm 2.22$  ‰ is calculated for the total recovered water samples (Figure 4). Although this is slightly heavier than the measured initial water

composition, if the errors are taken into account, there exists a difference of only 0.45 ‰ between the two. Therefore, the water transfer and collection protocols used for these experiments do not seem to result in significant fractionation of the total water sample composition. This means that any fractionations observed are the result of the sublimation process itself, and not the result of the experimental procedures themselves.

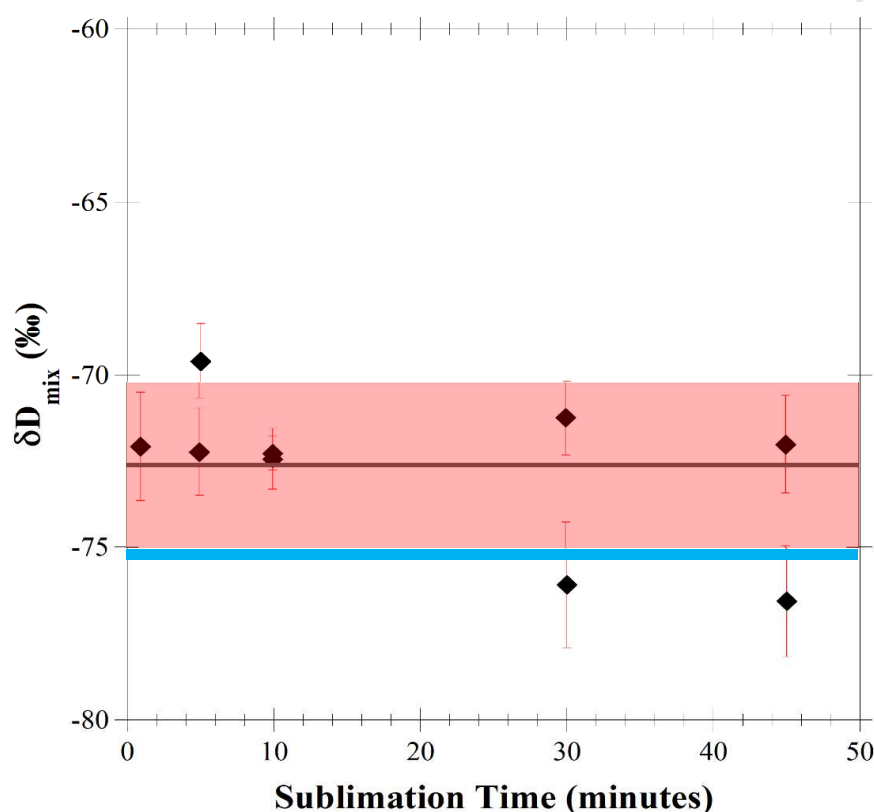


Figure 4: Isotopic mass balance calculated results (black diamonds), with the average value represented by the horizontal black line at -72.73 ‰. Standard deviation from this average is outlined by the pink box. The composition of the initial water used is shown using the blue horizontal line at -75.69 ‰, with the error smaller than the line width.

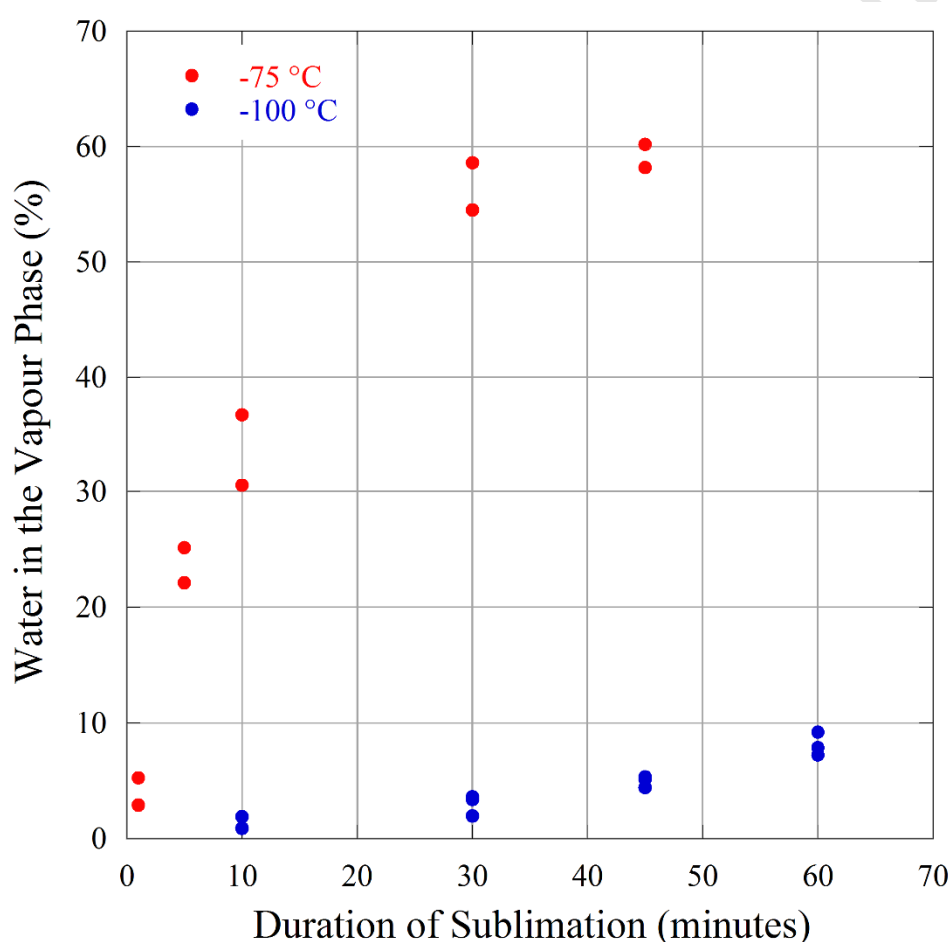
### 3. Results

Results derived from this study are collated in Appendix Table A1

#### 3.1. Rates of Sublimation

The first point to note is that sublimation occurs readily at -75 °C, even under relatively low vacuum conditions of  $10^{-3}$  mbar, which is close to the vapour pressure of ice at this temperature anyway. In fact, the percentage of water in the vapour phase rises rapidly from approximately 5 % at 1 minute duration, to around 33 % after ten minutes. However, beyond this, the rate of sublimation appears to reduce, most likely as a consequence of more water being released into the vapour phase than can be

trapped down and collected, resulting in increased pressure in the extraction line, limiting the amount of further sublimation that can occur after around 10 minutes (Figure 5). However, up to 10 minutes sublimation duration, the rate appears to be linear with time. This is also true for sublimation at  $-100^{\circ}\text{C}$  at  $10^{-5}$  mbar, where (again at the vapour pressure of ice at this temperature) the sublimation rate is much lower than is the case at  $-75^{\circ}\text{C}$ , resulting in lower amounts of water being released into the vapour phase across the same timescales and thus enabling sublimation to continue unhindered.



**Figure 5: Amount of Sublimation, measured as a percentage of the total water aliquot lost to the vapour phase at different time intervals.** N.B: data at  $-75^{\circ}\text{C}$  were collected under  $10^{-3}$  mbar pressure, whereas data at  $-100^{\circ}\text{C}$  were collected at  $10^{-5}$  mbar.

Taking the average percentages of water in the vapour phase for each time interval, and only plotting the data for experiments unaffected by non-removal of water vapour from the system, the true difference between sublimation rates can be seen (Figure 6). With the sublimation rate at  $-75^{\circ}\text{C}$  almost 30 x greater than the rate at  $-100^{\circ}\text{C}$ , despite both sets of experiments being conducted just

inside the temperature and pressure conditions needed to permit sublimation to occur, this demonstrates the strong temperature dependence on the sublimation process.

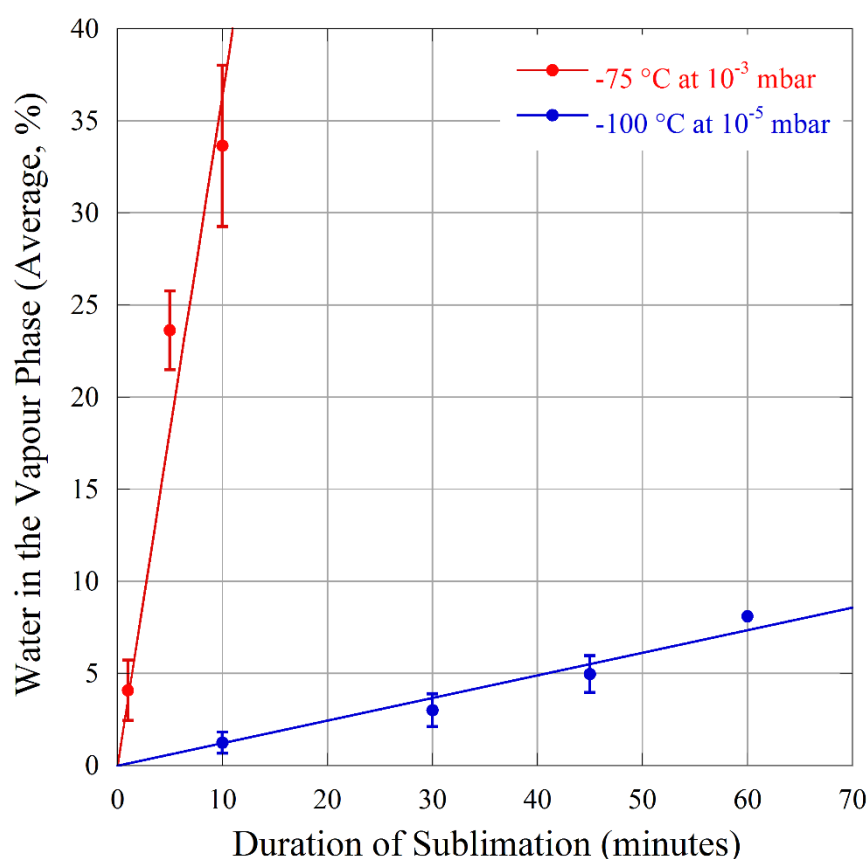


Figure 6: Rates of sublimation at water ice vapour pressures at different temperatures  
( $y_{-75, \text{red}} = 3.64x$ ,  $y_{-100, \text{blue}} = 0.12x$ )

To investigate the effect of pressure on the rate of sublimation, a second set of experiments were performed at -75 °C, at the lower pressure of 10<sup>-5</sup> mbar to compare with those collected at 10<sup>-3</sup> mbar (see Figure 7). What is immediately clear is that there is no significant difference in the rate of sublimation between the two pressures, one of which is 2 orders of magnitude lower than the vapour pressure of the water ice sample itself. This suggests that, so long as the pressure is low enough for sublimation to occur at the temperature in question, the actual pressure itself is irrelevant.

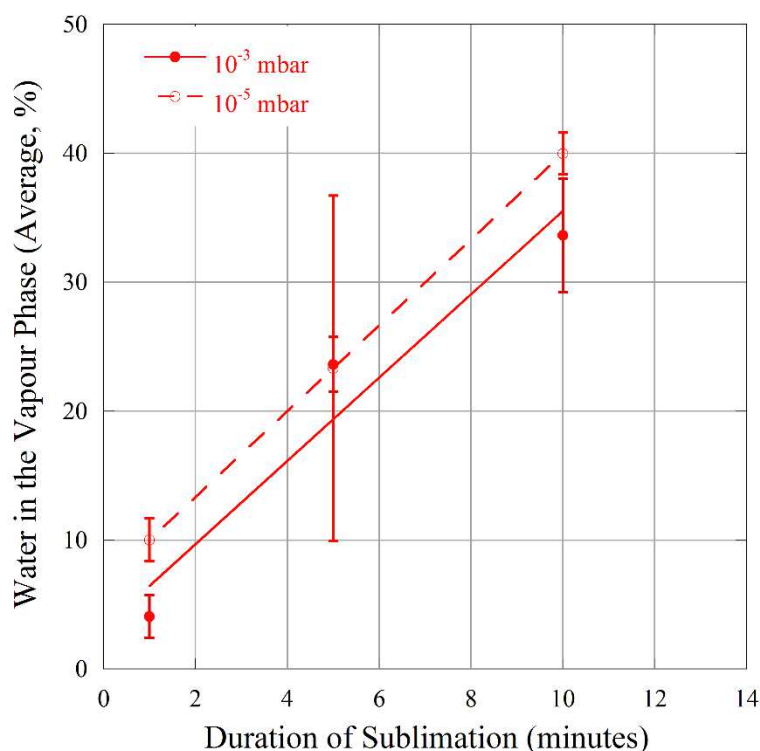


Figure 7: The percentage of water ice lost to the vapour phase at different pressures (additional lower pressure data are presented as red open circles with a dashed trend line). For  $10^{-3}$  mbar data,  $y_{\text{solid red}} = 3.23x$ , and for  $10^{-5}$  mbar,  $y_{\text{dashed red}} = 3.32x$ .

### 3.2. Isotopic Composition of the Sublimate and Residue Subsamples

Having established that a change in pressure has only a very minor effect on the rate of water ice loss to the vapour phase in comparison to a change in temperature, the effect of both of these variables on the extent of isotopic fractionation (both in the sublimate, and in the residual ice sample), if any, should also be characterised.

From a purely theoretical viewpoint, isotopic fractionation may not be expected to occur at all, given the fact that at such low temperatures as those of interest to this study, diffusion rates of D in water ice are so slow that the sublimated water vapour should remain at an essentially identical isotopic composition to the starting water ice D/H value. However, since significant fractionation has indeed been observed during sublimation (Lécuyer et al., 2017), it could be the case that although the bulk of the water ice solid itself is not undergoing fractionation, diffusion may be taking place within the boundary sublimating water layer, which may be closer to a liquid and could permit much more rapid diffusion and isotopic homogenisation than the more solid water ice below this layer. Under the low

pressure experimental conditions used for this study, water vapour is rapidly removed away from this sublimating boundary layer, thus preventing any possible vapour-solid reverse equilibration from occurring.

Unlike for the relative proportions of water in the vapour phase versus remaining in the residual ice sample, which can be back-calculated given the excellent recovery rates of water from this vacuum system, when it comes to measurements of isotopic composition, a certain minimal volume of water is required for an analysis to be performed. Further, although in theory it is possible to calculate the composition of the unanalysed component using Equation 2 outlined above, even with a small error on the measured component's isotopic composition, this can translate into almost infinite possibilities for the composition of the missing component, especially if this unanalysed component is below 1-2 % of the total water ice starting mass.

Therefore, the following isotopic data are not so numerous as the percentage abundance data and even where measurements were possible, they should be treated with caution, particularly for samples collected after short durations and/or samples representing a small percentage of the total water ice mass.

The first and most obvious result is that there is in general good agreement between the measured isotopic compositions of water vapour samples taken at both pressures, meaning that pressure does not seem to be the factor governing fractionation behaviour during sublimation (Figure 8). Another obvious trend is that the isotopic composition of the water lost to the vapour phase evolves over time as sublimation progresses, becoming progressively more enriched in D relative to H as sublimation continues. What is perhaps unexpected is that from an initial starting ice composition of -75.69 ‰, for the first few minutes of sublimation, the water ice lost to the vapour phase is enriched in lighter H relative to D, only switching to preferential loss of D compared to H after 10-30 minutes, which corresponds to approximately 40-50 % loss of the original water ice mass to the vapour phase. This switchover point in sublimation fractionation behaviour at -75 °C is clearly seen in Figure 8, where, at water losses below approximately 35 %, measured isotopic compositions at both pressures are lighter

(i.e. enriched in H relative to D) than the starting composition (red horizontal bar), and by 40-50 % water in the vapour phase and above, isotopic compositions are enriched in D relative to H.

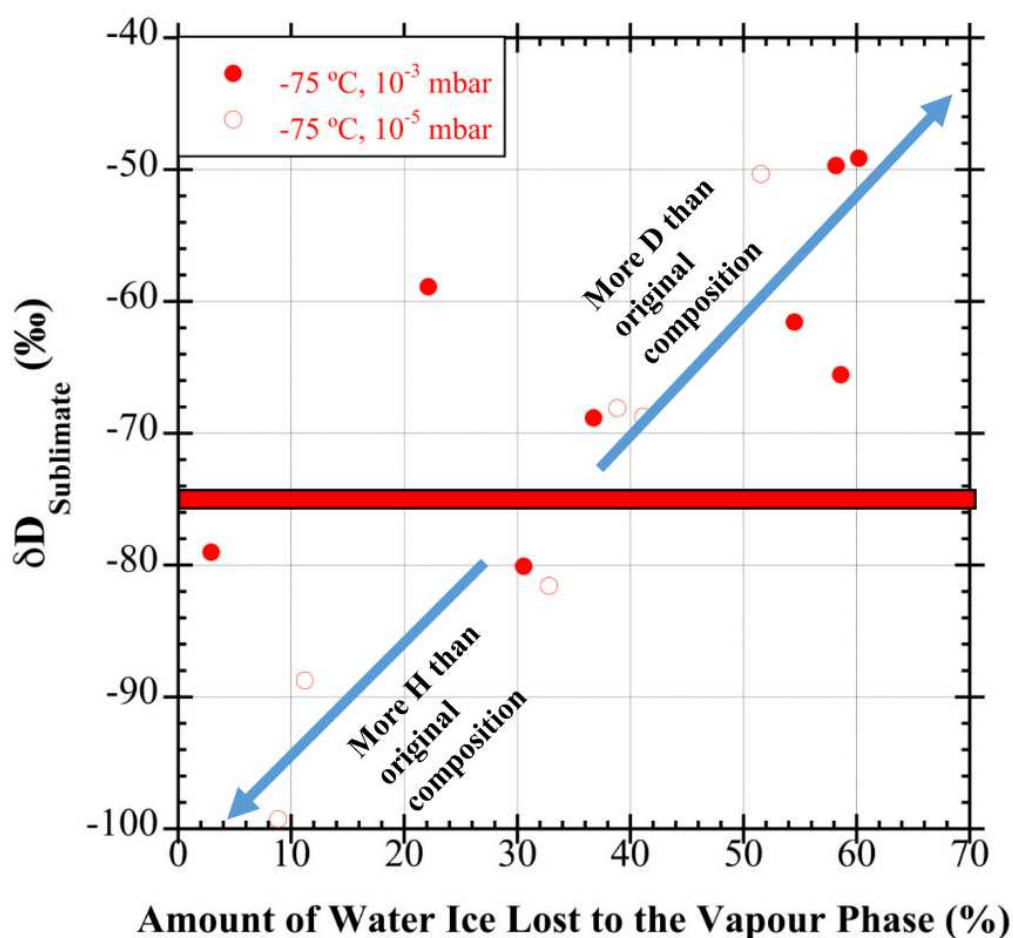
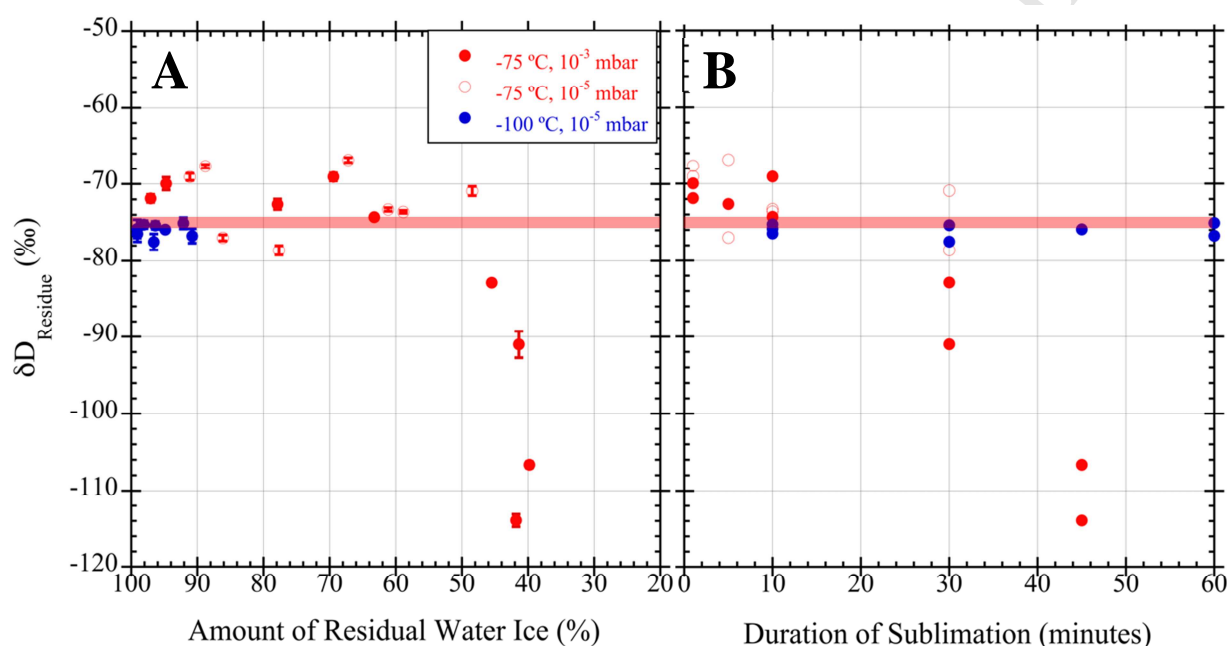


Figure 8: Measured Isotopic Composition of Water Lost to the Vapour Phase (starting composition shown as red horizontal bar)

Of greater importance to the aims of ESA's PROSPECT package is an understanding of the extent and nature of any changes to the residual water ice fraction, since this represents the actual sample that will be delivered to the ProSPA instrument for isotopic analysis. As already demonstrated, the amount of water ice lost to the vapour phase reduces to only several percent when the temperature is dropped from -75 °C to -100 °C, even across a timescale of tens of minutes up to one hour. This corresponds to around 90 % of the starting water content still being preserved in the sample after sitting at -100 °C for 1 hour. Further, at the lunar surface, temperatures will be even lower, with a specification that the drilling and transfer processes should not heat the sample above -150 °C. Following the trends observed in this study, that should result in the preservation of well over 90 % of the original water ice abundance within the analysed sample.

Correspondingly, changes to the isotopic compositions of the residual ice fractions are much less dramatic than is the case for the vapour phase fraction, remaining close to the starting composition until significant loss to the vapour phase depletes the residual ice abundance to around 50-65 % of its original mass (Figure 9). Again, taking into account the slow rate of sublimation that is likely under PROSPECT nominal operating conditions, this suggests that the residual water ice fraction analysed by ProSPA will not have undergone significant isotopic fractionation ( $< \pm 10$  ‰) within a timeframe of several hours.



**Figure 9: Evolution of the isotopic composition of the residual water ice fraction with A) the percentage of original water ice mass remaining, and B) the duration of sublimation, compared to the starting isotopic composition (red horizontal bars).** Note that in A), water ice loss up to 50 % of the original abundance will result in negligible isotopic fractionation of the remaining water ice, and in B), at temperatures below -100 °C, it will take at least 5 hours for ongoing sublimation to reach the tipping point of 50 % water ice loss after which significant isotopic fractionation of the residual water ice is expected.

### 3.3. Comparison of results from this study with previous work

The present study funded by ESA in support of its PROSPECT package follows an earlier study into the effects of sublimation on the isotopic fractionation of water ice also carried out in the same laboratory in Lyon, using the same glass vacuum line and elemental analyser for D/H isotopic analysis. The results from this previous study have already been published (Lécuyer et al., 2017), so it is useful to place the current dataset into context by comparing it with this earlier work.



In their earlier work, Lécuyer et al. used several different starting waters to produce their ice samples, and conducted experiments across a wider range of temperatures. For the sake of closer comparison, this paper is only concerned with their results at  $-75^{\circ}\text{C}$  obtained using Lyon doubly-distilled Rhône river water, with a starting composition of  $-70.3 \pm 0.8 \text{ ‰}$ , similar to the starting composition used for the new experiments outlined in this work.

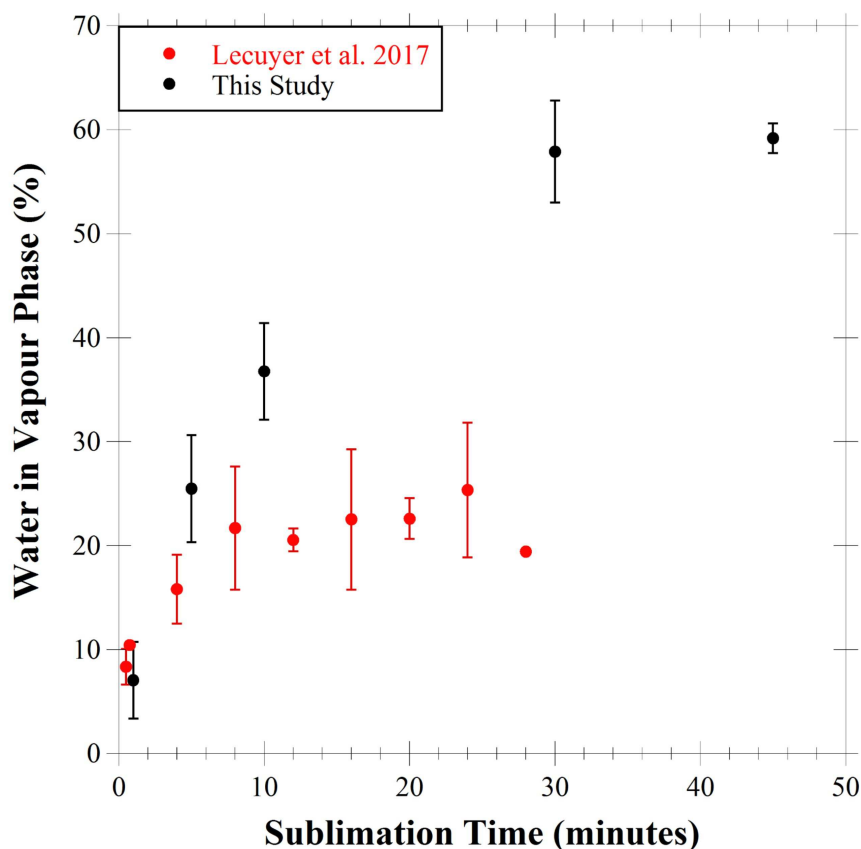


Figure 10: Comparing the amount of water ice lost to the vapour phase during sublimation in two separate studies using the same vacuum system.

Figure 10 plots the  $-75^{\circ}\text{C}$  data from Lécuyer et al. with the  $-75^{\circ}\text{C}$  data obtained at  $10^{-3}$  mbar and  $10^{-5}$  mbar in the present study. What is immediately apparent is that although both studies resulted in the same amount of sublimation occurring in the first few minutes, the earlier Lécuyer et al. study data begin to plateau after 8 minutes, whereas in the present study sublimation continues unabated for longer, although it too reaches a plateau after approximately 30 minutes. In both cases, this can be attributed to water vapour building up in the vacuum above the sublimating water ice sample, resulting in a local water ice loss-water vapour refreezing cycle, thereby hindering further net sublimation. The present study benefitted from a larger liquid nitrogen cooled water vapour trap and

resistance wire heating a much larger section of the glass vacuum line than did the earlier study, which results in more water vapour being removed from the system before it can build up to such a level near the water ice sample that it begins to refreeze back down onto the sublimating ice and reach a steady cycle of loss and retrapping.

Similarly, the isotopic compositions of the residual water ice fractions in the two studies display broadly similar trends with increasing sublimation; in both data sets, residual water ice fractions begin closer than  $\pm 10$  ‰ to their respective initial water isotopic compositions (see the horizontal red and black bars in Figure 11). Both then display the same trend towards increasingly H-rich residual ice compositions as sublimation progresses, although in both cases, this can be linked to the point at which the amount of water ice lost to the vapour phase begins to plateau. Once the amount of water ice lost to the vapour phase becomes too great for the water vapour trapping/removal measures in place to deal with, the isotopically-light, H-rich initial water vapour releases (see Figure 8) are able to mix with the remaining water ice mass at, or near to, the original isotopic composition, resulting in an increasingly H-rich residual ice composition.

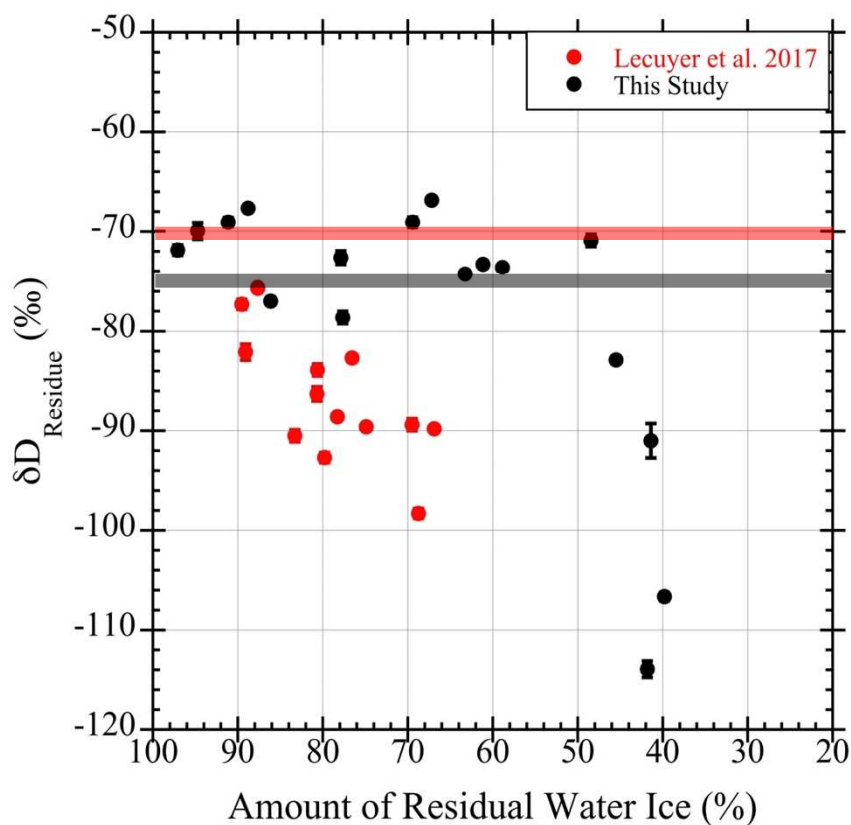


Figure 11: Evolution of the isotopic composition of the residual water ice fraction compared to the original starting water compositions for both studies.

#### 4. Conclusions

The experimental results described in this study are both consistent with previous work and reveal important insights which can be applied to the specific conditions that ESA's PROSPECT package is likely to be operating under when it performs its water ice and other volatiles investigations at the lunar surface in the near future.

Firstly, the rate of water ice loss to the vapour phase during sublimation has been shown to reduce dramatically with progressively lower temperatures, and this effect is largely independent of the pressure at which this is occurring. In other words, so long as the pressure is low enough for sublimation to occur at the temperatures in question, reducing the pressure further will not result in an increase in sublimation rate, but reducing the temperature will result in a reduction in sublimation rate. Although the base pressure limits of the vacuum system used in this study prevented sublimation experiments at -150 °C, looking at the reduction in sublimation rate between -75 °C and -100 °C, it can be suggested that at the PROSPECT working temperature guideline of -150 °C, sublimation rates will be so low that it would take at least several hours rather than minutes for a significant percentage of water ice to be lost. So, for the purposes of PROSPECT, even a sample drilling and transfer procedure that warms up a regolith sample to -150 °C for several hours is not going to result in a major loss of the water ice ProSPA is aiming to measure. This is in agreement with the results of previous studies to derive estimates of sublimation rates for water ice *via* first principles calculations (e.g. Andreas, 2007), which suggest that a small ng-sized sample of water ice may be heated to 150 K at the lunar surface for over two hours before losing a significant proportion of its mass to sublimation.

Related to the limited loss of water ice through sublimation is the associated limited fractionation of the residual water ice fraction that will be measured by ProSPA. This study suggests that up to 50 % of the original water ice abundance can be lost to sublimation before the remaining water ice in the drilled regolith sample becomes significantly fractionated ( $> \pm 10 \text{ ‰}$  compared to its true 'undisturbed' isotopic composition).

However, one aspect of the real PROSPECT lunar surface activities that this study cannot provide guidance for relates the potential role of the regolith grains themselves in altering the sublimation characteristics (stability and isotopic fractionation behaviour) of any lunar water ice frozen onto or weakly bound onto regolith mineral grain surfaces. In a Martian and cometary context, adsorption onto and diffusion of water vapour through fine-grained regoliths have been determined to be important factors governing stability of water ice (Bryson et al., 2008; Chevrier et al., 2008; Moores et al. (2012) have shown that the presence of regolith particles can have a large effect on the sublimation behaviour of water ice, compared to experiments run in the same way with only pure water ice, where increasing proportions of dust mixed into the water ice sample results in increased fractionation, favouring the adsorption of HDO onto dust grains, thereby preferentially losing lighter H<sub>2</sub>O to the vapour phase and resulting in the residual water ice becoming increasingly isotopically heavy, or enriched in D relative to H, as sublimation progresses. Clearly, in the PROSPECT lunar context, similar behaviour would result in an extremely fractionated residual ice isotopic composition, as water ice at or near to the lunar poles is only thought to make up between 1-10 wt%, with the remaining 90-99 % of the sample mass being made up of regolith particles. Therefore, the characterisation of the impact of the presence of regolith particles in a water ice sample under vacuum undergoing sublimation is an ongoing effort for the various groups involved in PROSPECT, with experiments under way to attempt to address this issue and take the results of this study further, including efforts to improve the water vapour removal method/trapping efficiency to permit sublimation to continue unhindered to even higher percentages of water ice loss.

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561 **Appendix Table A1:**

Pressure (mbar)	Sublimation Temperature (°C)	Sublimation Time (mins)	Initial Water (g)	Initial D/H (‰)	± (‰)	Sublimate (g)	Sublimate D/H (‰)	± (‰)	Residue (g)	Residue D/H (‰)	± (‰)	Sublimate + Residue (g)	Recovery %	Sublimation %	Residue %
10 <sup>-3</sup>	-75	5	0.69659	-75.69	0.29	0.17668	\	\	0.5261	\	\	0.70278	100.89	25.14	74.86
10 <sup>-3</sup>	-75	5	0.72599	-75.69	0.29	0.15415	-58.88	0.42	0.54272	-72.64	0.67	0.69687	95.99	22.12	77.88
10 <sup>-3</sup>	-75	10	0.66603	-75.69	0.29	0.20224	-80.09	0.37	0.45977	-69.09	0.52	0.66201	99.40	30.55	69.45
10 <sup>-3</sup>	-75	10	0.67225	-75.69	0.29	0.2469	-68.83	0.31	0.42504	-74.3	0.19	0.67194	99.95	36.74	63.26
10 <sup>-3</sup>	-75	30	0.67585	-75.69	0.29	0.36846	-61.55	0.74	0.30763	-82.88	0.34	0.67609	100.04	54.50	45.50
10 <sup>-3</sup>	-75	30	0.67928	-75.69	0.29	0.39775	-65.56	0.09	0.28094	-91	1.73	0.67869	99.91	58.61	41.39
10 <sup>-3</sup>	-75	1	0.67535	-75.69	0.29	0.03549	\	\	0.64017	-69.96	0.82	0.67566	100.05	5.25	94.75
10 <sup>-3</sup>	-75	1	0.6658	-75.69	0.29	0.01948	-79.01	1.06	0.64611	-71.88	0.51	0.66559	99.97	2.93	97.07
10 <sup>-3</sup>	-75	45	0.69909	-75.69	0.29	0.42144	-49.13	1.01	0.27868	-106.65	0.41	0.70012	100.15	60.20	39.80
10 <sup>-3</sup>	-75	45	0.71427	-75.69	0.29	0.41587	-49.69	0.79	0.29895	\	\	0.71482	100.08	58.18	41.82
10 <sup>-5</sup>	-100	60	0.55395	-75.69	0.29	0.05101	\	\	0.50294	-76.74	0.94	0.55395	100	9.21	90.79
10 <sup>-5</sup>	-100	10	0.50689	-75.69	0.29	0.0047	\	\	0.50219	-76.45	1.04	0.50689	100	0.93	99.07
10 <sup>-5</sup>	-100	10	0.51844	-75.69	0.29	0.0047	\	\	0.51374	-75.82	1.19	0.51844	100	0.91	99.09
10 <sup>-5</sup>	-100	60	0.51768	-75.69	0.29	0.04078	\	\	0.4769	-75.09	0.72	0.51768	100	7.88	92.12
10 <sup>-5</sup>	-100	30	0.57016	-75.69	0.29	0.02072	\	\	0.54944	-75.37	0.5	0.57016	100	3.63	96.37
10 <sup>-5</sup>	-100	30	0.52651	-75.69	0.29	0.01793	\	\	0.50858	-77.52	1.05	0.52651	100	3.41	96.59
10 <sup>-5</sup>	-100	10	0.51215	-75.69	0.29	0.00976	\	\	0.50239	-75.27	0.52	0.51215	100	1.91	98.09
10 <sup>-5</sup>	-100	45	0.5472	-75.69	0.29	0.0281	\	\	0.5191	-75.91	0.33	0.5472	100	5.14	94.86
10 <sup>-5</sup>	-100	45	0.57994	-71.68	0.78	0.03094	\	\	0.549	\	\	0.57994	100	5.34	94.66
10 <sup>-5</sup>	-100	45	0.5676	-71.68	0.78	0.02517	\	\	0.54243	\	\	0.5676	100	4.43	95.57
10 <sup>-5</sup>	-100	60	0.53754	-71.68	0.78	0.03886	\	\	0.49868	-76.55	0.19	0.53754	100	7.23	92.77
10 <sup>-5</sup>	-100	30	0.54651	-71.68	0.78	0.01089	\	\	0.53562	\	\	0.54651	100	1.99	98.01
10 <sup>-5</sup>	-75	10	0.53626	-71.68	0.78	0.20826	-68.09	0.36	0.32799	-73.31	0.23	0.53625	100.00	38.84	61.16
10 <sup>-5</sup>	-75	10	0.51969	-71.68	0.78	0.21425	-68.74	0.4	0.3068	-73.62	0.19	0.52105	100.26	41.12	58.88
10 <sup>-5</sup>	-75	5	0.5477	-71.68	0.78	0.07586	\	\	0.47187	-76.98	0.39	0.54773	100.01	13.85	86.15
10 <sup>-5</sup>	-75	5	0.56456	-71.68	0.78	0.18546	-81.57	0.09	0.37992	-66.86	0.32	0.56538	100.15	32.80	67.20
10 <sup>-5</sup>	-75	1	0.52362	-71.68	0.78	0.04648	-99.25	0.28	0.47859	-69.08	0.46	0.52507	100.28	8.85	91.15
10 <sup>-5</sup>	-75	30	0.55112	-71.68	0.78	0.28478	-73.64	0.27	0.26779	-70.92	0.6	0.55257	100.26	51.54	48.46
10 <sup>-5</sup>	-75	30	0.70456	-71.68	0.78	0.15701	-50.33	0.64	0.54594	-78.62	0.61	0.70295	99.77	22.34	77.66
10 <sup>-5</sup>	-75	1	0.5221	-72.01	2.21	0.05764	-88.74	0.1	0.45696	-67.67	0.24	0.5146	98.56	11.20	88.80

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**Mortimer et al. 2018: Highlights**

- Sublimation rate at low temperatures is very slow, independent of pressure
- 50% of the water ice can sublime before residual ice is significantly fractionated
- Samples kept  $<-150^{\circ}\text{C}$  will not experience significant water ice loss for many hours